



# Development of a continuous hydrogen generator fueled by ammonia borane for portable fuel cell applications

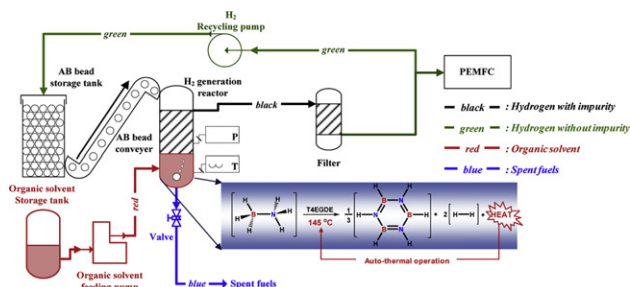
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## HIGHLIGHTS

- ▶ A novel  $H_2$  generator fueled by ammonia borane is developed.
- ▶ Dehydrogenation of ammonia borane is achieved by solvent-mediated thermolyses.
- ▶ The  $H_2$  generator shows fast load-following capability and rapid response time.
- ▶ The  $H_2$  generator produces  $H_2$  autothermally to operate a 200 W<sub>e</sub> PEMFC stack.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Thermally-induced dehydrogenation from a mixture of ammonia borane (AB) and a chemical promoter, tetraethyleneglycol dimethylether (T4EGDE) (AB:T4EGDE = 79:21, wt%) has been demonstrated as an efficient method for hydrogen production at 85–145 °C. We further build on these prior results to create a continuous  $H_2$  generator fueled by solid AB beads. The as-developed  $H_2$  generator releases ca. 2 equiv of hydrogen autothermally during operation by utilizing excess heat produced from AB dehydrogenation without any external heater. A purifying system equipped with acidic filter materials is further utilized to remove gaseous byproducts other than hydrogen. The  $H_2$  generator shows a rapid  $H_2$ -release rate up to 3.3 l( $H_2$ ) min<sup>-1</sup> with fast load-following capability. The as-developed  $H_2$  generator is ultimately integrated with a commercial 200 W<sub>e</sub> polymer electrolyte membrane fuel cell (PEMFC) to test its capability.

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## 1. Introduction

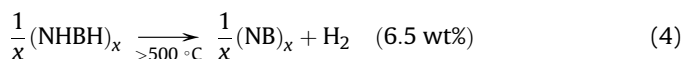
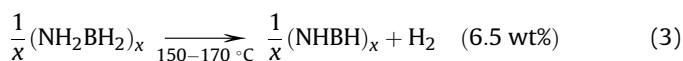
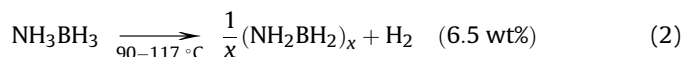
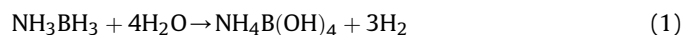
Chemical hydrides such as ammonia borane ( $NH_3BH_3$ , AB), sodium borohydride ( $NaBH_4$ , SBH), and carbosilanes have attracted considerable attention as hydrogen storage materials for fuel cell applications. Among these chemical hydrides, aqueous SBH solutions have been widely studied as a potential fuel to produce

hydrogen via hydrolysis in the presence of a number of heterogeneous catalysts based on cobalt boride [1], nickel boride [2], Pt–LiCoO<sub>2</sub> [3], Ru [4] and so forth. A hydrogen production system utilizing SBH solutions offers a number of advantages including: (i) fast  $H_2$ -release kinetics, (ii) facile control for  $H_2$ -release rate, and (iii) no formation of gaseous byproducts. A hydrolysis-based  $H_2$  generation system, however, requires a large quantity of water to dissolve SBH and further needs a base stabilizer (e.g., NaOH) to prevent autohydrolysis of the SBH fuel, leading to a decrease in hydrogen storage density to 7.3 wt% [5]. In addition, the hydrolyzed byproducts possess thermodynamically stable B–O bonds that are costly to regenerate [6].

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Due to its high hydrogen storage density (19.6 wt%), ammonia borane (AB) has been recently recognized as a promising hydrogen storage material for transportation applications [7–10]. Hydrogen can be released from AB by either hydrolysis (Eq. (1)) or thermolysis (Eq. (2)) under mild conditions.



As in the case of SBH, hydrolytic  $\text{H}_2$ -release properties from AB have been extensively studied [11–13], and these studies have demonstrated that  $\text{H}_2$  can readily be produced even at room temperature with various metal catalysts. However, the solubility of AB in water has been shown to be much lower than that of SBH, implying that the theoretical hydrogen storage capacity of an aqueous AB solution should be limited below 4.9 wt%, unless the water is recycled. Moreover, AB hydrolysis has also resulted in the formation of spent-fuels containing B–O bonds, along with ammonia, which are detrimental to PEMFC [14], making a hydrolysis-based system employing AB less attractive.

In contrast, AB thermolyses can release a large quantity of  $\text{H}_2$  at  $<250^\circ\text{C}$  with a material-based hydrogen storage capacity of ca. 13.5 wt% upon releasing about 2 equiv of hydrogen [15,16]. Exhaustive  $\text{H}_2$ -release from AB is undesirable particularly for transportation applications since tremendous amounts of energy are required to regenerate the resulting byproduct, boron nitride, into AB [17], even though AB has a maximum  $\text{H}_2$  storage density of 19.6 wt% upon producing 3 equiv of  $\text{H}_2$  through reactions (Eqs. (2)–(4)). In addition, Miranda and Ceder previously calculated the values of  $\Delta H$  for Eqs. (2) and (3) at 0 K to be  $-6.57$  and  $-40.1 \text{ kJ mol}^{-1}$ , respectively, and further exhibited that these reactions were exergonic at various temperatures ranging from 0 to 600 K based on DFT studies [18]. Moreover, Devarakonda reported that Eqs. (2) and (3) were exothermic; the AB dehydrogenation reaction produced heat of  $22 \text{ kJ mol}^{-1}$  for the first equivalent of  $\text{H}_2$  and heat of  $15 \text{ kJ mol}^{-1}$  for the second equivalent of  $\text{H}_2$  [19]. Due to the exothermicity of AB dehydrogenation [18,19], the heat required for  $\text{H}_2$  generation from AB can readily be achieved from AB dehydrogenation itself and/or obtained from the waste heat of exhaust gas from a PEMFC. Pure AB thermolyses, however, have been shown to have drawbacks such as: (i) slow  $\text{H}_2$ -release kinetics with an induction period, (ii) formation of impurities and scatters, and (iii) foaming of AB upon dehydrogenation [20]. The slow kinetics of pure AB thermolyses can be enhanced by employing chemical promoters such as proton sponge (PS) [21], diammoniate of diborane (DADB) [22], nano-phase boron nitride [23], and ionic liquids [7,21,24]. In addition, acid and base catalysts have also been found to enhance  $\text{H}_2$  release kinetics [8,9]. Organic solvents [25] and mesoporous silica [10] have been utilized to suppress the formation of impurities and scatters. Furthermore, methyl cellulose has been previously employed to prevent the identified AB foaming during dehydrogenation [26].

By building on these advances, new concepts associated with a continuous  $\text{H}_2$  generator fueled by AB have been proposed. Varma and co-workers have recently reported on the concept of non-catalytic hydrothermolysis [27,28] and have demonstrated that a remarkably enhanced hydrogen storage capacity of ca. 14 wt% can

be achieved from pristine AB thermolyses via effective reaction heat management [29]. The authors reported that these hydrothermal and/or thermal methods produced a number of byproducts including boric acid, polyborazine, polyiminoborane, tetra-coordinated boron atoms, polyaminoborane, and cyclotriborazane [27,28]. In particular, the regeneration of boric acid would again need energy-extensive regeneration processes. Moreover, these hydrothermal methods involved high pressure build-up (ca. 19 bar) resulting from sudden hydrogen evolution [27], which implies that a heavy and high pressure-resistant storage tank is necessary for these approaches, thereby decreasing a system-based hydrogen storage capacity. Despite these issues, however, the hydrothermal concept could be applied to stationary power generation where the system-based weight limits are less concerning than those in transportation applications. Another plausible strategy for continuous  $\text{H}_2$  generation from AB has been demonstrated by the co-use of ionic liquids (e.g., 1-butyl-3-methylimidazolium chloride, bmimCl) as both transporting media of AB and promoters for AB dehydrogenation [20,30]. For example, mixtures of AB and bmimCl (AB: bmimCl = 50:50, wt%) were reported to exhibit  $>2$  equiv of  $\text{H}_2$  with solid products [20]: this concept was suggested to potentially meet the 2015 DOE system-based target of 5.5 wt% (system-based  $\text{H}_2$  yield) for transportation applications [31]. In order to ensure facile feeding of the AB/bmimCl mixtures, however, the content of the ionic liquid should be higher than 50 wt%. In addition, the mixtures became solid following dehydrogenation of  $>1$  equiv of  $\text{H}_2$ , which could cause potential clogging problems [20].

We report here on a novel  $\text{H}_2$  generator utilizing solid AB beads, an organic promoter, an AB conveyer with a spinning wheel system, and an external  $\text{H}_2$  purification system. The performance of the  $\text{H}_2$  generator was evaluated by integrating it with a commercial 200 W<sub>e</sub> polymer electrolyte membrane fuel cell (PEMFC) stack. The as-developed  $\text{H}_2$  generator proved capable of enabling the production of  $\text{H}_2$  continuously at  $3.3 \text{ l}(\text{H}_2) \text{ min}^{-1}$  to power the 200 W<sub>e</sub> PEMFC stack with fast load-following capability and rapid response time during the PEMFC operation. Plausible strategies for improving the efficiency of the  $\text{H}_2$  generator are discussed in conjunction with findings.

## 2. Experimental

### 2.1. Materials

AB (Aviator, 98%) was ground into fine powder using a commercial grinder under an atmosphere of  $\text{N}_2$ . The AB powder was then pelletized into beads in a spherical shape by a manual dry pressing process. Note that this process could be accomplished by an automatic pelletizing machine. The AB beads possessed a weight of ca. 0.082 g with a diameter of 5.7 mm. The density of the AB bead was nearly identical to that of an AB crystal ( $0.74 \text{ g cm}^{-3}$ ) [32]. The theoretical quantity of hydrogen that could be produced from one AB bead was calculated to be ca. 130 ml( $\text{H}_2$ ), with an assumption that 2 equiv of  $\text{H}_2$  would be released from the AB bead. Tetraethyleneglycol dimethylether (T4EGDE, Sigma Aldrich, 99%) was used as-received and kept under a  $\text{N}_2$  environment.

### 2.2. Hydrogen production from AB beads and characterization of spent-fuels

To design a continuous reactor fueled by AB, thermally-induced  $\text{H}_2$ -release properties of the AB beads should be understood. In this context, dehydrogenation reactions with the AB beads at various temperatures were initially conducted in a modified glass reactor (volume, 40 ml) possessing three necks (two for inlets and one for outlet). One inlet was used to feed the AB beads and the second

inlet was employed to purge the reactor with N<sub>2</sub> gas. During consecutive H<sub>2</sub> generation tests, the AB pellets were supplied manually through the first inlet at targeted intervals. The outlet was utilized to discharge byproduct gases into two traps, one filled with T4EGDE and the other with water. Following the removal of byproducts in the traps at 0 °C, the purified H<sub>2</sub> was supplied into a gas burette system for real-time measurement of the rate of H<sub>2</sub>-release as well as the accumulative amount of H<sub>2</sub>. The overall experimental apparatus for H<sub>2</sub> measurement is shown in Fig. 1. Material-based H<sub>2</sub> yields and system-based H<sub>2</sub> yields were calculated using the following Eqs. (5) and (6).

$$\text{H}_2 \text{ yield (wt\%, material based)} = \frac{\text{weight of H}_2 \text{ produced}}{\text{weight of reactants (AB beads + solvent)}} \quad (5)$$

$$\text{H}_2 \text{ yield (wt\%, system based)} = \frac{\text{weight of H}_2 \text{ produced}}{\text{weight of total system (reactants, trap and system hardware)}} \quad (6)$$

Upon dehydrogenation of the AB beads, qualitative analyses of the gaseous byproducts were performed in situ using an FT-IR spectrometer (Nicolet iS10, Thermo Scientific) equipped with an MCT detector and a customized gas cell. Spectral data were collected using a scan rate of 16 scans min<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>. Solid and/or liquid spent-fuels remaining in the reactor were dissolved in T4EGDE of 0.5 ml and further characterized using <sup>11</sup>B NMR spectroscopy. <sup>11</sup>B NMR spectra were recorded using a 600 MHz FT-NMR Varian spectrometer while calibrated with an external reference, BF<sub>3</sub>OEt<sub>2</sub> ( $\delta$  = 0.0 ppm).

### 2.3. Procedure for H<sub>2</sub> production with a continuous H<sub>2</sub> generator

A continuous H<sub>2</sub> generator fueled by the AB beads was designed based on the obtained results above, as depicted in Fig. 2. This hydrogen production system consisted of: (i) an AB bead storage/conveying system, (ii) a semi-batch-type H<sub>2</sub> generation reactor, (iii) a solvent storage/supply system (drawn in red), (iv) an external purifier, and (v) a H<sub>2</sub> recycling pump (drawn in green). The AB storage tank possessed a maximum storage capacity of 82 g of AB beads (1000 ea). In the conveyer, a spinning wheel system was utilized to feed the AB beads from the AB storage tank into the H<sub>2</sub>

generation reactor [33]. Feeding rates of the AB beads could be adjusted within a range of 0.0–2.3 g min<sup>-1</sup>. The H<sub>2</sub> generator made of two-folded titanium metal had an inner volume of 300 ml. Besides an inlet for the conveyed AB beads, a reactor outlet was employed to discharge generated hydrogen with byproduct gases. A filter containing chemical adsorbents of acidic-activated carbon (3M, Multi gas/vapor cartridge 6006) was designed to remove potential undesired gases through chemical reactions, and positioned at the outlet of the reactor. Note that the solvent (T4EGDE) storage/supply system and a spent-fuel discharging system

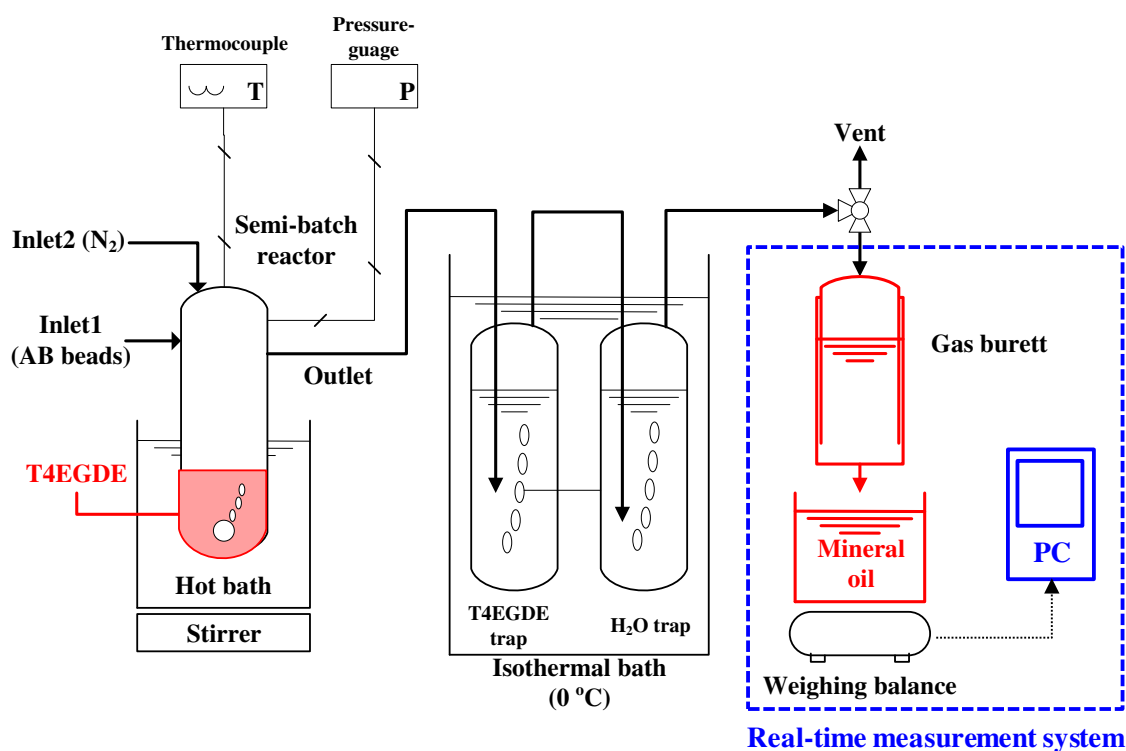
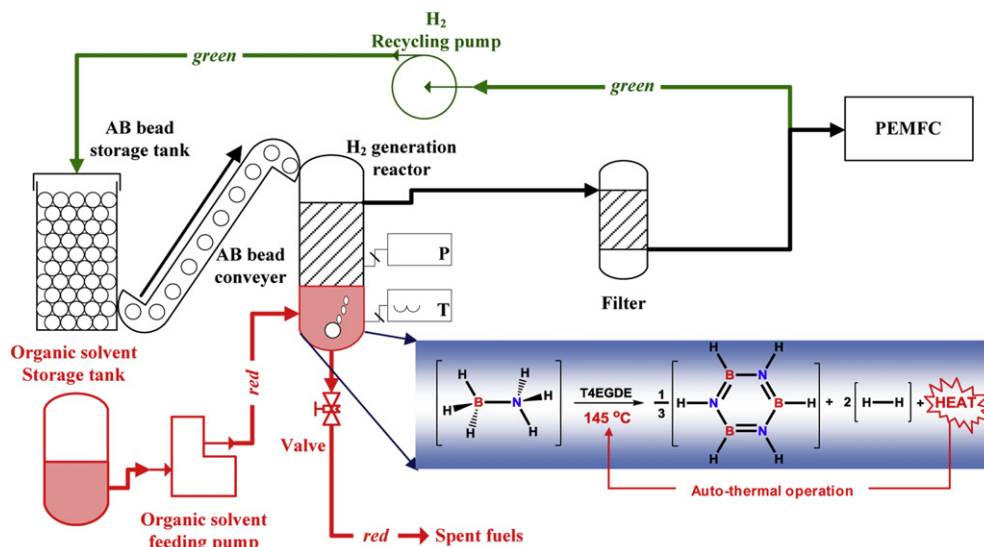


Fig. 1. Schematic diagram of the experimental apparatus for H<sub>2</sub> measurement.



**Fig. 2.** A process flow diagram of the continuous H<sub>2</sub> generator from AB. Components drawn in red were not included in this study (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

depicted in Fig. 2 (drawn in red), were not demonstrated in this study, although these system would eventually be necessary for long-term operation; instead, a sufficient amount of T4EGDE (120 g) was pre-loaded into the reactor, prior to hydrogen production. The AB storage tank was purged by recycled hydrogen from a trap (*vide infra*) into the AB storage tank to prevent backflow of the partially evaporated organic solvent, T4EGDE, and gaseous byproducts from the reactor. The constructed H<sub>2</sub> generator is depicted in Fig. 3 (For interpretation of the references to color in this paragraph, the reader is referred to the web version of this article.).

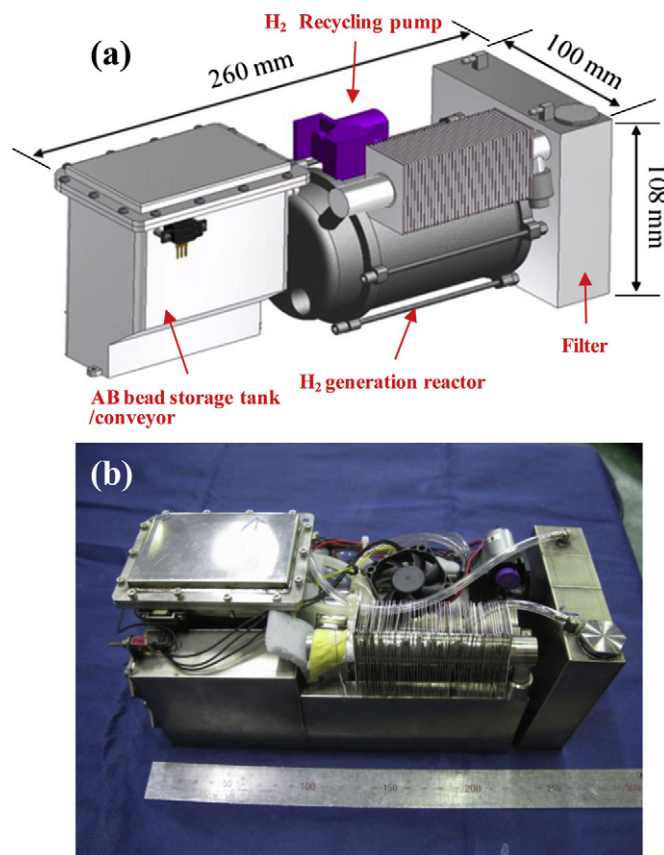
The procedure for H<sub>2</sub>-release on demand from this AB-based H<sub>2</sub> generator is described below. Desired amounts of the AB beads were kept in the storage tank, thermally isolated from the reactor. The AB beads were then consecutively supplied into the H<sub>2</sub> generation reactor filled with pre-heated T4EGDE at 130–150 °C. A K-type thermocouple was inserted into the reactor to monitor the reactor temperature during the AB dehydrogenation reactions. Outlet gases from the reactor were additionally purified in the external purifier. Rates of H<sub>2</sub> generation were directly measured by a mass flow meter (MFM, TSM-120 MKP). The as-developed H<sub>2</sub> generator was ultimately connected to a commercial 200 W<sub>e</sub> PEMFC stack (H-200, Horizon Fuel Cell Technologies). The current loading of 7 A in the stack was conducted by a DC load (EL-500P, DAE GIL).

### 3. Results and discussion

#### 3.1. Solvent-mediated H<sub>2</sub> release properties from the AB beads

To develop an efficient and continuous reactor fueled by AB for long-term applications, we created a concept for a semi-batch-type reactor utilizing AB beads, as illustrated in Fig. 2. To examine the potential viability of this reactor concept, H<sub>2</sub>-release kinetics and exothermicity for the dehydrogenation of the AB beads along with characterization of impurities, needed to be analyzed. In this context, dehydrogenation reactions with the AB beads at various temperatures were initially conducted in a modified glass reactor in which the AB beads were delivered manually. The rates of H<sub>2</sub>-release from the pristine AB bead at temperatures in a range of 85–145 °C are shown in Fig. 4a. Consistent with a previous report [22],

H<sub>2</sub> was rarely released at 85 °C within 60 min. The rate of dehydrogenation, however, increased as reaction temperature increased, while the induction period became shorter. Within 60 min, the AB bead liberated ca. 1.0 equiv of H<sub>2</sub> with an induction period of 10 min at 105 °C, while 1.3 equiv of H<sub>2</sub> was released at 125 °C with an induction period of 3 min. The H<sub>2</sub> release kinetics using the AB beads improved drastically, giving 1.9 equiv of H<sub>2</sub> at



**Fig. 3.** (a) 3-D sketch and (b) photograph of AB-based H<sub>2</sub> generator.



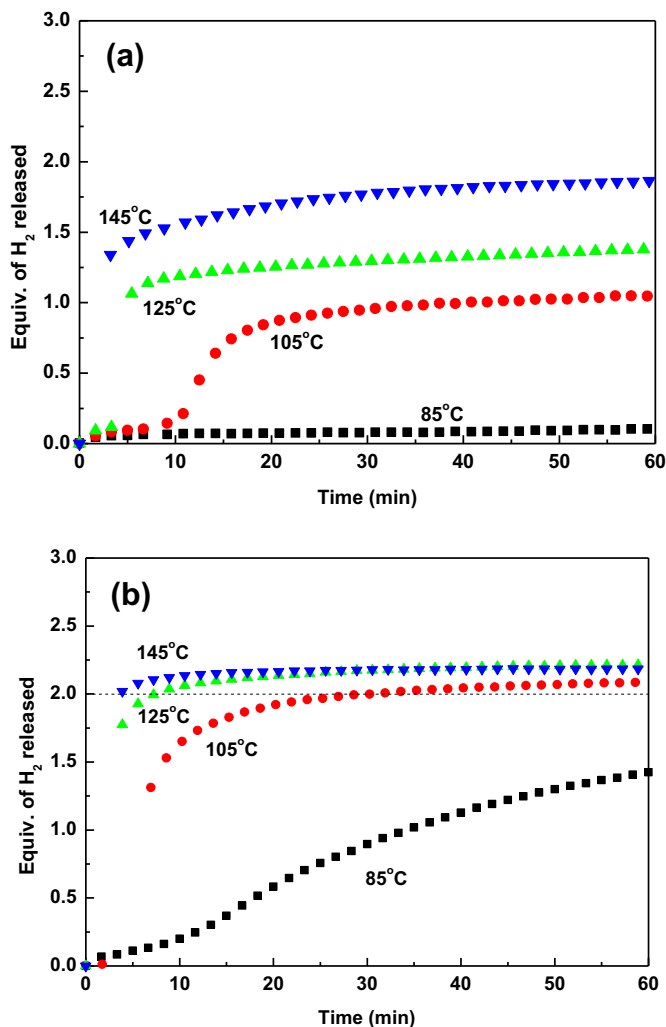


Fig. 4. H<sub>2</sub> release from (a) pristine AB bead and (b) AB bead with T4EGDE (AB:T4EGDE = 14:86, wt%) at (■) 85 °C, (●) 105 °C, (▲) 125 °C, and (▼) 145 °C.

145 °C within 60 min with no induction period. The rates of H<sub>2</sub>-release associated with using pristine AB beads, however, still need to be improved in order to minimize reactor size, facilitate start-up, and enhance dynamic response for the realization of a continuous H<sub>2</sub> generator applicable to fuel cell applications. In addition, we found that considerable foam formed during dehydrogenation, indicating that H<sub>2</sub> release from pure AB materials is unfavorable. Sneddon and co-workers previously found that the dehydrogenation rate of a mixture of AB and T4EGDE (50:50, wt%) was much faster than that with pristine AB powders, producing >2 equiv of hydrogen at 85 °C over 240 min, and that the time required for the release of >2 equiv of H<sub>2</sub> from the AB and T4EGDE blend was shortened to 120 min at 95 °C [24]. Likewise, we recently discovered that H<sub>2</sub>-release rates from AB powders could be promoted in the presence of small amounts of a polyetheral solvent (e.g., T4EGDE) as an additive (29 wt% relative to AB + solvent).

To apply the solvent-assisted AB activation process to a continuous H<sub>2</sub> generator, T4EGDE was chosen among the useful polyetheral solvent promoters because it possesses a high boiling point of ca. 275 °C [34]. This physical property of T4EGDE solvent helps to prevent not only its backflow into the AB storage tank but also its inflow into the filtering system due to vaporization, a process potentially hazardous for the long term operation of a fuel cell system. Note that due to the exothermic nature of the reaction [19],

the reactor temperature is likely to increase continuously during AB dehydrogenation and could reach higher than 150 °C (*vide infra*). An additional point to note about our approach is that the reactor was preloaded with heated T4EGDE solvent before the AB pellets were added. This step was taken instead of initially mixing AB with T4EGDE since liquid T4EGDE solvent can be exuded during the pelletizing process.

The H<sub>2</sub>-release rates obtained from the AB bead in T4EGDE (AB:T4EGDE = 14:86, wt%) were found to be significantly faster than those in the absence of the solvent (Fig. 4b). For example, 1.4 equiv of H<sub>2</sub> was released within 60 min with no induction period at 85 °C (Fig. 4b). Moreover, >2 equiv of H<sub>2</sub> was readily achieved within 7.3 and 3.6 min at 125 °C and 145 °C, respectively, from AB bead mixed with T4EGDE (14:86, wt%). However, excess amounts of T4EGDE retarded the rates of H<sub>2</sub>-release from the AB bead (Fig. 5). To illustrate, the AB bead/T4EGDE mixture (14:86, wt%) produced 2 equiv of H<sub>2</sub> within 7.3 min at 125 °C while a bead with a ratio of AB:T4EGDE = 3:97 (wt%) gave 2 equiv of H<sub>2</sub> for ca. 30 min at the same temperature (Fig. 5a, inset). The rate of H<sub>2</sub>-release from AB beads/T4EGDE blends can be further improved by sustaining an optimal composition between AB and T4EGDE with the continuous supplying of T4EGDE into the reactor, as suggested in Fig. 2 (relevant components are drawn in red). Following the removal of byproducts from the reactor, the fresh organic solvent can be re-introduced into the reactor (Fig. 2, drawn in red). In this way, the initial kinetics of the AB dehydrogenation can be enhanced even at a lower

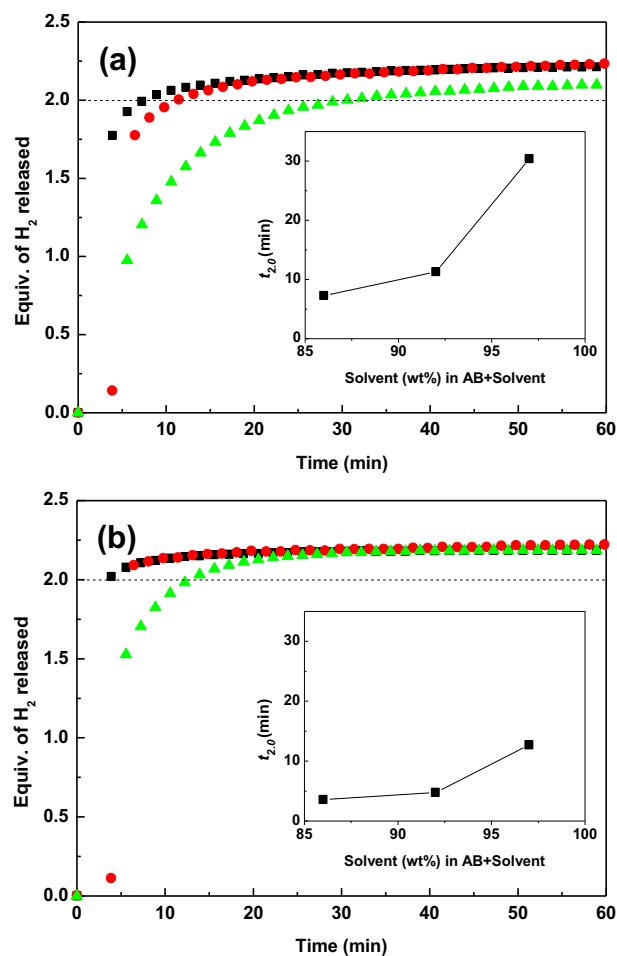


Fig. 5. H<sub>2</sub> release from AB bead mixed with T4EGDE and  $t_{2,0}$  (inset) in different ratios: (■) 86 wt%, (●) 92 wt%, and (▲) 97 wt% with respect to AB + T4EGDE at (a) 125 °C and (b) 145 °C.  $t_{2,0}$  is defined as the time required for the release of 2 equiv of H<sub>2</sub>.

temperature (e.g., 125 °C) without the suppression of H<sub>2</sub>-release rate from excess solvent. In this study, we increased reaction temperatures to enhance H<sub>2</sub>-release kinetics since temperatures higher than 145 °C can readily be achieved by excess heat produced from exothermic dehydrogenation of AB (*vide infra*). Similar to dehydrogenation with AB powders, the time ( $t_{2,0}$ ) required to produce 2.0 equiv of H<sub>2</sub> from AB was shorter at a higher temperature; e.g., with a ratio of AB:T4EGDE = 3:97,  $t_{2,0}$  was determined to be 12.7 min at 145 °C as compared to 30 min at 125 °C (Fig. 5b, inset) (For interpretation of the references to color in this paragraph, the reader is referred to the web version of this article.).

Consecutive hydrogen generation via the T4EGDE-mediated AB thermolytic decomposition was also conducted at 145 °C, as shown in Fig. 6. Fifteen AB beads with a total weight of 1.23 g were successively supplied into the reactor with pre-loaded T4EGDE (0.5 g) to ultimately produce ca. 1.7 l (H<sub>2</sub>) at 145 °C, which corresponds to a H<sub>2</sub> yield of 8.9 wt% based on material (weight of AB + T4EGDE). These repeated processes showed fast H<sub>2</sub>-release kinetics, with 2 equiv of H<sub>2</sub> being released within ca. 12 min for the 1st bead and within ca. 20 min for the 15th bead. In the case of the 15th bead, >1.8 equiv of H<sub>2</sub> was released for 10 min. These results clearly indicate that H<sub>2</sub> flow rates can easily be controlled by the feeding rate, and the proposed reactor concept is feasible for the continuous operation needed to power a PEMFC.

### 3.2. Performance of the as-developed, continuous H<sub>2</sub> generator in powering a 200 W<sub>e</sub> PEMFC

Based on the obtained results above, a continuous hydrogen production system possessing an AB storage tank with a maximum storage capacity of 82 g of AB beads (ca. 1000 ea), a fuel conveyer, a semi-batch-type reactor, and an external purifier was constructed (Fig. 3). Brooks et al. previously proposed a pristine AB bead-based reactor concept employing an auger transport system [35]. Along with the auger transport system, a spinning wheel system adopted in the as-developed H<sub>2</sub> generator is an alternative that can prevent potential problems associated with fuel delivery upon transporting AB beads from the fuel tank to the H<sub>2</sub> generation reactor. The spherical shape of the AB bead works well to minimize the formation of blockages which can frequently occur during solid feeding. In addition, the highly compacted AB beads produced by dry pressing led to an increase in hydrogen storage capacity due to the absence of void volume, as compared to AB powders [30]. Another distinctive characteristic of the H<sub>2</sub> generation reactor is to

utilize T4EGDE, an organic solvent, as a promoter. With the capability to enhance H<sub>2</sub>-release kinetics of AB, the T4EGDE promoter can provide the additional benefit of dissolving scattered and gaseous byproducts produced during AB dehydrogenation. Moreover, the solvent additive can help render spent-fuels fluidic to remove them easily from the reactor by inducing a pressure difference between the inner and outer zones. The identified role of T4EGDE in the continuous reactor is to: (i) promote H<sub>2</sub> release kinetics, (ii) dissolve scatter and foaming generated from AB, and (iii) fluidize the solid products from AB thermolyses.

To design a byproduct sequestration system, undesired gaseous products were analyzed by in situ FT-IR spectroscopic techniques. The T4EGDE-assisted AB thermolyses afforded borazine as the dominant gas byproduct following AB dehydrogenation at 145 °C. Since these compounds can be vaporized and delivered with hydrogen into a PEMFC, an external purifying system is essential for eliminating any byproducts that potentially deactivate a PEMFC. The as-developed system utilized a chemical trap to remove undesired byproduct gases. Most of the produced solid scatters and gaseous byproducts were sieved physically and further sequestered by neutralization of basic byproducts in the chemical trap filled with acidic solid materials. In addition, the H<sub>2</sub> recycling pump was designed to pump a portion of the purified hydrogen through the AB bead storage tank into the reactor in order to suppress the back-flow of gaseous byproducts from the reactor to the AB storage tank. This design feature is advantageous since the added T4EGDE promoter can still evaporate back into the AB storage tank under normal operating conditions despite its high boiling point (*vide supra*). This vaporized solvent can dissolve the surface of the solid AB pellets, thereby resulting in failure of feeding. The recycling pump is thus necessary for long term applications.

Controlling the flow rate of the purified hydrogen is also important to maximize the efficiency of the as-developed H<sub>2</sub> generator by enhancing fast start-up and dynamic response. The H<sub>2</sub> flow rate for a fuel cell can potentially be regulated by the AB feeding rate. With this in mind, additional thermolyses of the AB beads were conducted using different AB feeding rates. Prior to feeding, the reactor containing T4EGDE was preheated to 150 °C by an external heater. As depicted in Fig. 7, the flow rates of the resulting, purified hydrogen proved to be controllable by adjusting the feeding rate of the AB beads. Upon adjusting the AB feeding rates from 0.49 g min<sup>-1</sup> (6 ea min<sup>-1</sup>) to 1.2 g min<sup>-1</sup> (14 ea min<sup>-1</sup>) to 2.0 g min<sup>-1</sup> (24 ea min<sup>-1</sup>), flow rates of the produced H<sub>2</sub> were determined to be 0.73, 1.7, and 3.0 l(H<sub>2</sub>) min<sup>-1</sup>, respectively, with subtle fluctuations (Fig. 7). These measured flow rates were in good agreement with those calculated based on the assumption that 2 equiv of H<sub>2</sub> would be produced from the AB beads, thus indicating that regardless of AB feeding rates, ca. 2 equiv of hydrogen per AB was produced in the presence of the T4EGDE promoter under the reaction conditions. Response times, defined as the time required to produce H<sub>2</sub> at the calculated flow rate (based on the assumption that 2 equiv of H<sub>2</sub> per one AB bead would be produced), for hydrogen production with changes in AB feeding rates were observed to be approximately 2 min. The temperature of the reactor increased continuously from 152 °C, but leveled off to 175 °C after 15 min as the AB feeding rate increased from 0.49 to 2.0 g min<sup>-1</sup>, which is again due to the exothermicity of the AB dehydrogenation; i.e., faster rates of reaction with increased feeding rates produced hydrogen with more amounts of excess heat. This result implies that AB dehydrogenation can auto-thermally proceed even at a lower feeding rate with improved heat insulation. To prevent overheating of the reactor, external coolers should be employed because excess heat induces evaporation of the organic solvent. Therefore, proper heat insulation is needed to sustain the reaction temperature within a desired range (140–

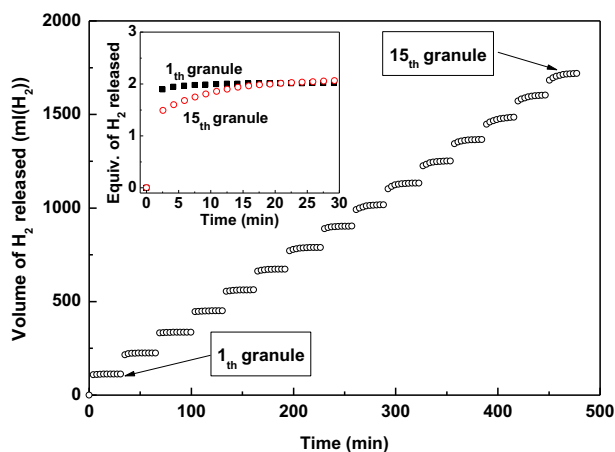


Fig. 6. The consecutive H<sub>2</sub>-release profile based on the T4EGDE-mediated thermolyses of AB beads at 145 °C. H<sub>2</sub>-release profiles of 1st bead (■) and 15th bead (○) were compared (inset).

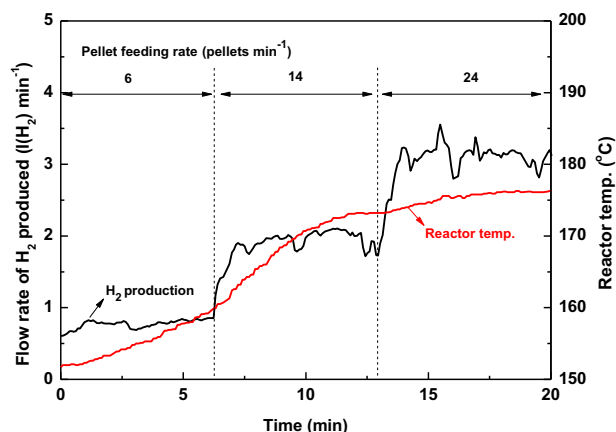


Fig. 7. Changes inflow rates of the produced  $H_2$  and the reactor temperature depending on the feeding rates of AB beads (black line: flow rate of  $H_2$  produced; red line: reactor temperature) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

160 °C) since the absence of external coolers in this reactor concept compromises system efficiency.

The identified  $H_2$ -release properties of the AB beads via T4EGDE-mediated AB thermolyses strongly suggest that the as-developed generator can supply hydrogen on-demand to a continuous fuel cell application. To evaluate performance of the as-developed  $H_2$  generation system for fuel cell applications, the AB-fueled  $H_2$  generator was integrated with a commercial 200  $W_e$  PEMFC stack running at a current of 7 A. The reactor pre-filled with T4EGDE (120 g) was initially heated to ca. 130 °C by an external heater. Following the removal of the external heater, the AB beads were supplied into the reactor with a feeding rate of 2.3 g  $min^{-1}$  (28 ea  $min^{-1}$ ). This feeding rate corresponded to an expected  $H_2$  production rate of 3.3 l( $H_2$ )  $min^{-1}$ , again calculated based on a hypothesis that 2 equiv of  $H_2$  would be produced. As depicted in Fig. 8, temperature in the reactor increased and reached a plateau at ca. 160 °C after 10 min upon continuous feeding of AB, indicating that sufficient amounts of waste-heat were produced to maintain autothermal operation for the fuel cell application. During operation, the pressure from the reactor to the PEMFC stack was

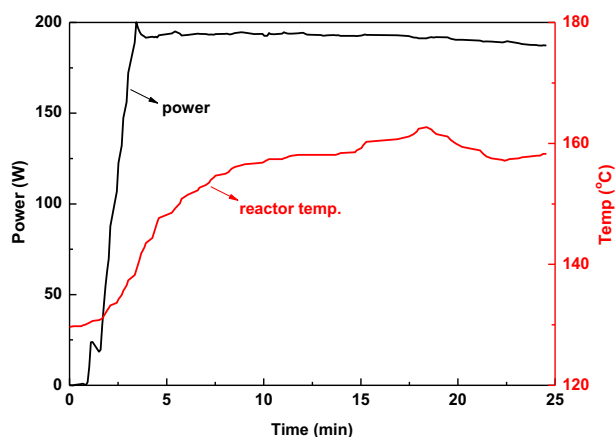


Fig. 8. Evolutions of power output from the 200  $W_e$  PEMFC stack upon dehydrogenation of mixtures of AB beads/T4EGDE and the reactor temperature during continuous operation (black line: flow rate of  $H_2$  produced; red line: reactor temperature) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

sustained at 55–60 kPa (gauge). Simultaneously, voltage of the stack increased to ca. 28 V at 7 A after 3 min, equivalent to a power output of 200  $W_e$  (Fig. 8). The obtained result from the as-developed  $H_2$  generator is nearly identical to the rated performance of a commercial stack fueled by pure hydrogen (28.8 V at 7 A) [36], indicating that the  $H_2$  generator produced sufficient quantities of  $H_2$  to operate the stack, and the purifying system effectively functioned to eliminate byproducts. This operation was stopped at 25 min owing to the following two reasons: (i) The motor linked with the conveyor was malfunctioned presumably due to its low, mechanical durability and (ii) the usable AB fuels were exhausted. Note that the currently used AB storage tank possesses an intrinsic dead volume of approximately 30% with respect to its total volume, and 70% of the initial AB pellets were consumed within 25 min. For prolonged operation, the currently used AB bead storage/conveying system needs to be improved by: (i) increasing the size of the AB tank while eliminating dead volume, and (ii) enhancing the durability of the electrical motor.

### 3.3. Eliminating byproducts from the outlet gases and discharging spent-fuels from the reactor

Performance of the AB-based, continuous  $H_2$  generator has been successfully demonstrated to power a 200  $W_e$  PEMFC. However, we identified two major issues that should be resolved for the development of an efficient, light-weight  $H_2$  generator: (i) purification of gaseous byproducts from downstream of the reactor and (ii) removal of spent-fuels from the reactor. To monitor the filtering capacity of the equipped sequestration systems, FT-IR spectroscopic studies were conducted following  $H_2$  production of AB dehydrogenation at 0.25 l( $H_2$ )  $min^{-1}$  (feeding rate of AB beads = 0.16 g  $min^{-1}$ ). Fig. 9 shows Gram–Schmidt intensities of the gases released during the T4EGDE-mediated AB thermolyses at 145 °C with and without filters as a function time. The Gram–Schmidt curves provide quantitative information on gases detected by the FT-IR spectrometer; i.e., a higher intensity indicates production of more amounts of gaseous byproducts. The curve obtained without the filters exhibits a sudden rise in the early stage (<10 min) of the dehydrogenation reaction and the increased intensity appears to be sustained after ~20 min (Fig. 9, red circle). A major gaseous byproduct was found to be a cyclic compound,

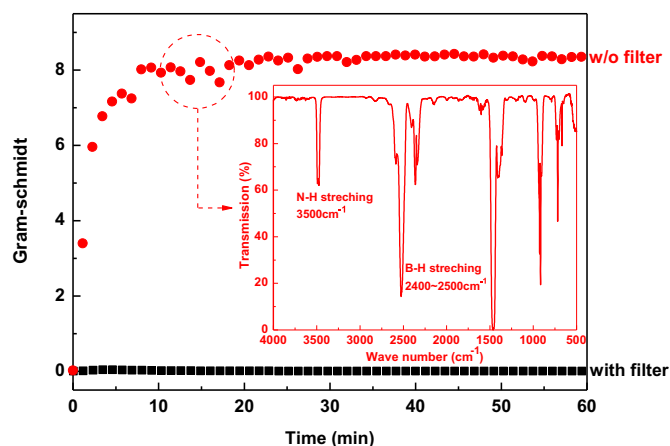


Fig. 9. FT-IR analyses of the released gases during T4EGDE-mediated thermolyses of AB at 145 °C with or without filtration: with filter (■) and without filter (●). The released gases without filtration mainly showed borazine in the FT-IR spectrum (inset) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

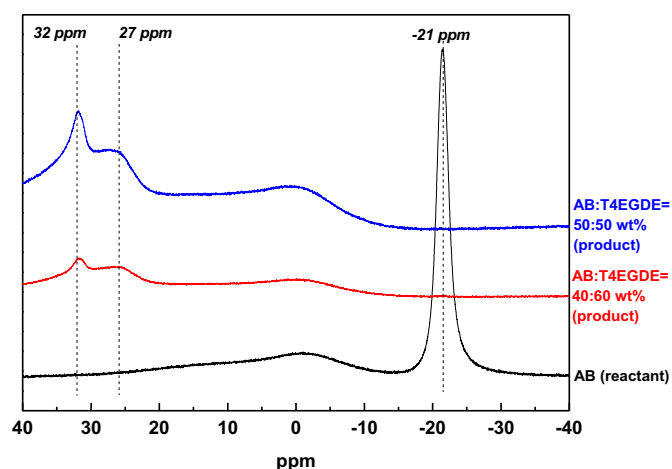


Fig. 10.  $^{11}\text{B}$  NMR spectra for the spent-fuels from mixtures of AB and T4EGDE in different ratios (AB:T4EGDE = 40:60 and 50:50, wt%).

borazine (Fig. 9 inset), as evidenced by FT-IR studies. Borazine ( $\text{B}_3\text{N}_3\text{H}_6$ ) is an inorganic analogue of benzene and known to be detrimental to PEMFCs possessing acidic proton exchange membranes [37]. In contrast, almost no byproducts were found upon utilization of a chemical trap containing acidic active carbons (Fig. 9, black rectangle). For complete removal, 1 g of the carbon materials was required to purify 1.8 l of hydrogen with impurities from the reactor at 145 °C and the trap capacity of the carbon materials can be defined as  $1.8 \text{ l}(\text{H}_2)\text{g}_{\text{trap}}^{-1}$  (For interpretation of the references to color in this paragraph, the reader is referred to the web version of this article.).

Effective discharging of spent-fuels is also important for designing an AB-based  $\text{H}_2$  generator. For the thermolysis reactions at 85 °C, pure AB powders are known to give linear and/or branched polyaminoborane (PAB) as well as polyiminoborane (PIB) as liquid and/or solid byproducts, depending on the extent of dehydrogenation [38]. The spent-fuels generally turned to solids after >2 equiv of  $\text{H}_2$  was released from AB, which makes a system utilizing pure AB solids less attractive along with their slow  $\text{H}_2$ -release kinetics. For facile discharging of the spent-fuels, waste-

fuels in a liquid form would be favored over those in a solid form. The spent-fuels appeared to remain fluidic even when the ratio of AB and T4EGDE reached 50:50 (wt%), but they were likely solidified upon supplying additional AB beads for dehydrogenation.  $^{11}\text{B}$  NMR spectra of the spent-fuels following dehydrogenation of the AB/T4EGDE mixtures (50:50 and 40:60, wt%) at 145 °C indicate the formation of polyborazylene ( $\delta = +27 \text{ ppm}$ ) as a solid waste-fuel as well as borazine ( $\delta = +32 \text{ ppm}$ ) at 145 °C (Fig. 10). The quantities of these products seem to increase with an increase in the AB/T4EGDE ratio. The chain length of polyborazylene likely increased to give solidified precipitation as dehydrogenation proceeded, which makes byproduct discharging difficult. Other solvents with higher capabilities to dissolve polyborazylene should thus be screened to develop an improved discharging system.

The required specification of an AB-fueled, continuous  $\text{H}_2$  generator to power a 200  $\text{W}_e$  fuel cell for >10 h is speculated and summarized in Table 1. Since no AB-fueled, continuous hydrogen system is now available, we fixed a desired total system weight to 3030 g, corresponding to  $607 \text{ W h kg}_{\text{system}}^{-1}$ , based on that of a commercial SBH-fueled PEMFC system (Horizon fuel cell, AEROPAK equipped with fuel cartridge type II, 2124 W h) with a specific energy density of  $607 \text{ W h kg}_{\text{system}}^{-1}$  as a reference. To achieve this goal, the weight of the current trap (1060 g) needs to decrease >50% to less than 530 g. This means that trap capacity ( $\text{l}(\text{H}_2)\text{g}_{\text{trap}}^{-1}$ , *vide supra*) of 1.8 should be increased to 3.6. This enhancement can be attained by increasing the surface area of the filtering materials as well as by impregnating more acidic material into pores while reducing volume and weight of the adsorbents. Secondly, the weight of the current system hardware (system weight except for AB, solvent, trap and stack, 1000 g) should further be reduced to <700 g. The desirable reduction in system weight can be achieved not only by utilizing light-weight components but also by eliminating unnecessary parts; e.g., the thickness of AB storage tank is currently 1 mm but could be further reduced to 0.5 mm while sustaining inner pressure of 1 bar. Lastly, the usage of an organic solvent could potentially be maintained below 29 wt% with respect to AB + solvent while dissolving solid products in the reactor for discharging, as suggested in Fig. 1 (drawn in red) (For interpretation of the references to color in this paragraph, the reader is referred to the web version of this article.).

Table 1

Targeted specifications of an AB-fueled PEMFC power-pack comparable to the commercial SBH-fueled PEMFC power pack (200  $\text{W}_e$ ).

|   | 200 $\text{W}_e$ AEROPAK system with fuel cartridge type II (2125 W h, horizon fuel cell) | Current AB-fueled system (based on current technology level) | Targeted AB-fueled system (expected) |
|---|---|--|--------------------------------------|
| Fuel  | Aqueous SBH solution  | AB bead:T4EGDE = 50:50 (wt%)                                 | AB bead:T4EGDE = 71:29 (wt%)         |
| Trap capacity ( $\text{l}(\text{H}_2)\text{g}_{\text{trap}}^{-1}$ )   | No need   | 1.8  | 3.6                                  |
| Total system weight except for the PEMFC stack <sup>a</sup> (g)       | 3030  | 4620   | 3030                                 |
|   | AB (g)  | 1280   | 1280                                 |
|   | Solvent (g)   | 1280   | 520                                  |
|   | Trap (g)  | 1060   | 530                                  |
|   | System hardware (g) <sup>b</sup>  | 1000   | 700                                  |
| Total weight (g)  | 3500  | 5090   | 3500                                 |
| Total system specific energy ( $\text{W h kg}_{\text{system}}^{-1}$ ) | 607   | 417  | 607                                  |
| System-based $\text{H}_2$ yield (wt%)                                 | 4.91  | 3.38   | 4.91                                 |

<sup>a</sup> Stack weight : 470 g.

<sup>b</sup> System hardware: system weight except for AB, solvent, trap and stack.



#### 4. Conclusions

In summary, a novel H<sub>2</sub> generator fueled by AB beads has been developed based on T4EGDE-assisted AB thermolyses, and integrated with a 200 W<sub>e</sub> PEMFC stack. The continuous H<sub>2</sub> generator utilized a spinning wheel system to supply solid AB beads, prepared by a conventional dry pressing process. The H<sub>2</sub> generator operating under ambient pressure proved its fast load-following capability and was further able to produce hydrogen up to 3.3 l(H<sub>2</sub>) min<sup>-1</sup>, sufficient to operate a 200 W<sub>e</sub> PEMFC stack. In addition, the as-developed H<sub>2</sub> generator employed the exothermic nature of the AB dehydrogenation to produce hydrogen autothermally without any external heater. The purifying system utilizing acidic materials successfully removed all gaseous byproducts (mostly borazine) to deliver pure H<sub>2</sub> into the 200 W<sub>e</sub> PEMFC stack. The as-developed system containing 58 g of AB beads (700 ea) exhibited its capability for continuous H<sub>2</sub> production for 25 min to power a commercial 200 W<sub>e</sub> PEMFC stack without significant deterioration. To our best knowledge, this is the first demonstration of the feasibility of AB-based continuous H<sub>2</sub> generator for a fuel cell application.

Despite these achievements, elimination of gaseous byproducts and discharging of the spent-fuels still need to be optimized to utilize the suggested reactor concept for long-term applications. In particular, development of a lightweight purifying system possessing high filtering capacity is necessary. With such improvements, the as-developed H<sub>2</sub> generator is expected to apply to medium and/or large-sized applications including powering unmanned aerial vehicle, portable power packs, and hydrogen station.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at <http://dx.doi.org/10.1016/j.jpowsour.2012.11.045>.

#### References

- [1] J. Lee, K.Y. Kong, C.R. Jung, E.A. Cho, S.P. Yoon, J. Han, T.-G. Lee, S.W. Nam, *Catal. Today* 120 (2007) 305–310.

- [2] K.A. Holbrook, P.J. Twist, *J. Chem. Soc. A* (1971) 890–894.
- [3] Y. Kojima, K. Suzuki, K. Fukumoto, M. Sasaki, T. Yamamoto, Y. Kawai, H. Hayashi, *Int. J. Hydrogen Energy* 27 (2002) 1029–1034.
- [4] S.C. Amendola, S.L. Sharp-Goldman, M.S. Janjua, N.C. Spencer, M.T. Kelly, P.J. Petillo, M. Binder, *Int. J. Hydrogen Energy* 25 (2000) 969–975.
- [5] H. Dong, H.X. Yang, X.P. Ai, C.S. Cha, *Int. J. Hydrogen Energy* 28 (2003) 1095–1100.
- [6] P.V. Ramachandran, P.D. Gagare, *Inorg. Chem.* 46 (2007) 7810–7817.
- [7] M.E. Bluhm, M.G. Bradley, R. Butterick III, U. Kusari, L.G. Sneddon, *J. Am. Chem. Soc.* 128 (2006) 7748–7749.
- [8] F.H. Stephens, R.T. Baker, M.H. Matus, D.J. Grant, D.A. Dixon, *Angew. Chem., Int. Ed.* 46 (2007) 746–749.
- [9] R.J. Keaton, J.M. Blacquiére, R.T. Baker, *J. Am. Chem. Soc.* 129 (2007) 1844–1845.
- [10] A. Gutowska, L. Li, U. Shin, C.M. Wang, X.S. Li, J.C. Linehan, R.S. Smith, B.D. Kay, B. Schmid, W. Shaw, M. Gutowski, T. Autrey, *Angew. Chem., Int. Ed.* 44 (2005) 3578–3582.
- [11] M. Chandra, Q. Xu, *J. Power Sources* 156 (2006) 190–194.
- [12] Q. Xu, M. Chandra, *J. Power Sources* 163 (2006) 364–370.
- [13] M. Chandra, Q. Xu, *J. Power Sources* 168 (2007) 135–142.
- [14] R. Halseid, P.J.S. Vie, R. Tunold, *J. Power Sources* 154 (2006) 343–350.
- [15] G. Wolf, J. Baumann, F. Baitalow, F.P. Hoffmann, *Thermochim. Acta* 343 (2000) 19–25.
- [16] F. Baitalow, J. Baumann, G. Wolf, K. Jaenicke-Rößler, G. Leitner, *Thermochim. Acta* 391 (2002) 159–168.
- [17] S. Damle, Development of regenerable, high-capacity boron nitrogen hydrides for hydrogen storage, in: DOE EERE Program Review (May 18, 2006), [http://www.hydrogen.energy.gov/pdfs/review06/stp\\_24\\_damle.pdf](http://www.hydrogen.energy.gov/pdfs/review06/stp_24_damle.pdf).
- [18] C.R. Miranda, G. Ceder, *J. Chem. Phys.* 126 (2007) 184703/1–184703/11.
- [19] M. Devarakonda, K. Brooks, E. Ronnebro, S. Rassat, *Int. J. Hydrogen Energy* 37 (2012) 2779–2793.
- [20] R.K. Ahluwalia, J.K. Peng, T.Q. Hua, *Int. J. Hydrogen Energy* 36 (2011) 15689–15697.
- [21] D.W. Himmelberger, C.W. Yoon, M.E. Bluhm, P.J. Carroll, L.G. Sneddon, *J. Am. Chem. Soc.* 131 (2009) 14101–14110.
- [22] D.J. Heldebrant, A. Karkamkar, N.J. Hess, M. Bowden, S. Rassat, F. Zheng, K. Rappe, T. Autrey, *Chem. Mater.* 20 (2008) 5332–5336.
- [23] D. Neiner, A. Karkamkar, J.C. Linehan, B. Arey, T. Autrey, S.M. Kauzlarich, *J. Phys. Chem. C* 113 (2009) 1098–1103.
- [24] D.W. Himmelberger, L.R. Alden, M.E. Bluhm, L.G. Sneddon, *Inorg. Chem.* 47 (2009) 9883–9889.
- [25] M.-K. Han, H.-J. Kim, Korean Patent, KR10-2009-0114035.
- [26] D. Choi, A.J. Karkamkar, S.T. Autrey, C.L. Aardahl, US Patent, US 2009/0302269.
- [27] M. Diwan, H.T. Hwang, A. Al-Kukhun, A. Varma, *AIChE J.* 57 (2011) 259–264.
- [28] H.T. Hwang, A. Al-Kukhun, A. Varma, *Ind. Eng. Chem. Res.* 49 (2010) 10994–11000.
- [29] H.T. Hwang, A. Al-Kukhun, A. Varma, *Int. J. Hydrogen Energy* 37 (2012) 2407–2411.
- [30] L. Aardahl, S.D. Rassat, *Int. J. Hydrogen Energy* 34 (2009) 6676–6683.
- [31] Ned T. Stetson, Hydrogen storage overview, in: DOE Annual Merit Review and Peer Evaluation Meeting (May 15, 2012) (2012), [http://www.hydrogen.energy.gov/pdfs/review12/st000\\_stetson\\_2012\\_o.pdf](http://www.hydrogen.energy.gov/pdfs/review12/st000_stetson_2012_o.pdf).
- [32] E.W. Hughes, *J. Am. Chem. Soc.* 78 (1956) 502–503.
- [33] Y. Kim, Y. Kim, Y. Kim, C.W. Yoon, S.-P. Yoon, S.W. Nam, S.A. Hong, J.H. Han, H.C. Ham, K. Kim, Korean Patent KR10-2012-0068200.
- [34] NIST, MML, Tetraglyme Boiling Point. <http://webbook.nist.gov/cgi/cbook.cgi?ID=C143248&Mask=4>.
- [35] K. Brooks, M. Devarakonda, S. Rassat, D. King, D. Herling, Proceedings of ASME 8th International Fuel Cell Science, Engineering and Technology Conference (2010), ISBN 978-0-7918-3875-4.
- [36] Horizon Fuel Cell Technologies, Standard Systems Specifications of Stacks. [http://www.horizonfuelcell.com/fuel\\_cell\\_stacks.htm](http://www.horizonfuelcell.com/fuel_cell_stacks.htm).
- [37] T.B. Marder, *Angew. Chem., Int. Ed.* 46 (2007) 8116–8118.
- [38] W.J. Shaw, J.C. Linehan, N.K. Szymczak, D.J. Heldebrant, C. Yonker, D.M. Camaioni, R.T. Baker, T. Autrey, *Angew. Chem., Int. Ed.* 120 (2008) 7603–7606.